Symmetry Groups for Unit Cells in Solids

JAMES J. P. STEWART
Stewart Computational Chemistry, 15210 Paddington Circle, Colorado Springs, Colorado 80921

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ABSTRACT: Two types of symmetry groups are commonly used in chemistry. Point groups are used for molecules, whereas, for solids, the 230 space groups are used. Neither of these types of symmetry groups are suitable for representing unit cells in solids, the symmetry of which is intermediate between that of point groups and space groups. To represent the symmetry of unit cells in an infinite lattice, a third type of symmetry group must be used. An algorithmic method of generating these symmetry groups is described. It can be demonstrated that these groups are valid by use of conventional symmetry group theory. This technique has been applied to the two-dimensional graphite lattice. Because the new method generates symmetry tables using only the topology of the system, the symmetry properties of graphs can also readily be derived. Last, the relationship between these groups and the other two types of groups is identified.
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Introduction

Symmetry in chemistry is usually restricted to two types of systems: individual molecules and ions, which are best represented using point-group theory; and extended systems, that is, solids, for which space-group theory is more appropriate.

In recent years, a semiempirical method, the cluster method, for rapidly calculating the electronic structure of polymers and solids, has been developed.[1] This method uses a large unit cell, typically composed of several fundamental unit cells. A prerequisite of this method is that the size of unit cell should be sufficiently large that the electronic structure at the Γ point in the Brillouin zone is an accurate representation of the entire system. To better represent the symmetries of the wave functions in the clusters, the symmetry properties of cluster groups[2] was investigated. Because the associated symmetry groups were obviously quite large, and, therefore, tedious to work with, algorithmic procedures have been developed to automate the generation and manipulation of these groups. This article addresses the theory involved

Correspondence to: J. J. P. Stewart; e-mail: jstewart@fai.com
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and provides some simple applications to the two-dimensional graphite lattice.

Conventional Symmetry Groups

POINT GROUPS

The number of point groups found in chemistry is quite limited. The complete set of single groups consists of the rotation groups C_n, C_{nv}, C_{nh}, S_n, D_n, and D_{nh}, in which n is usually less than 7 or 8; the seven cubic groups T, T_h, T_d, O, O_h, I, and I_h; two axial infinite groups, $C_{\infty v}$ and $D_{\infty h}$; and R_3, the group of the sphere. With the exception of R_3, the highest degeneracy of any single-point group is five, which is found in the icosahedral groups. A second less commonly used set of point groups is the double groups. In these, the effect of rotation by 360° is to reverse the sign of the associated eigenfunctions. Such groups are used when spin-orbit effects are important. In these groups, the highest degeneracy found is seen in the I_h' group, where the fivefold degenerate representation of the I_h group is split into a fourfold and a sixfold degenerate representation.

SPACE GROUPS

The number of possible space groups is even more limited. The most common set of single space groups is that for three-dimensional space; there are precisely 230 of these, each of which belongs to one of 14 Bravais lattices, each of which, in turn, belongs to one of the seven crystal systems. Systems that are unsymmetric to time reversal, such as the magnetically active systems, have their own space groups, similar to the double groups of point-group theory. These are the 1191 Shubnikov[3] black-and-white or magnetic space groups.

The range of point-group symmetries possible at each atom in a crystal is restricted by the Bravais lattice. In all, there are 32 possible site symmetries, ranging from C_i to O_h, for systems that are symmetric under time reversal, and an extra 58 for the other solids.

Unit Cells

Intermediate between the discrete and infinite systems are unit cells. These can be fundamental unit cells or multiples of the fundamental unit cell, and, in the discussion to follow, the term ''unit cell'' should be construed as referring to both fundamental unit cells and to multiples of it. The symmetry conventionally assigned to these unit cells is that of the associated space group. This description is completely valid for both the topology and electronic structure of the solid, but, as will be shown, is not suitable for describing the symmetries of the eigenfunctions of clusters.

Evidence for Existence of Other Groups

In recent years, methods have been developed to allow a fragment of an extended species to be used to model the full system. The ''cluster'' method[1,4] for example, uses a unit cell, frequently a multiple of the fundamental unit cell, and, by application of the Born–von Kármán[5] periodic boundary conditions, allows the electronic structure of the infinite system to be modeled. The electronic structures of these systems exhibit neither space-group nor point-group symmetries. The first indication of the presence of a new type of symmetry was provided by the electronic eigenfunctions. There, unexpected degeneracies were frequently encountered. In the case of two- and three-dimensional systems, these degeneracies frequently exceeded the highest degeneracy of any finite point group (five) and any little cogroup of any space group (six). Similarly, high degeneracies were observed when the electronic structure of ''coronene torrus'' was investigated by Hosoya et al.[6] In that work, the eigenvalues resulting from the application of π-electron theory to various clusters from the two-dimensional graphite layer were examined. In the case of a coronene-like cluster, the eigenvalues were integers and highly degenerate: ± 3; ± 2 (sixfold degenerate); ± 1 (threefold degenerate); and 0 (fourfold degenerate).

Clearly, the symmetry properties of clusters, and therefore the associated symmetry groups, are different from those of either point groups or space groups. More interestingly, because the number of clusters that can be used to represent any given system is infinite, the potential number of associated symmetry groups is also infinite.

Theory

Before embarking on the theory proper, a brief review of the properties of groups is necessary to

define the terms that will be used. This review uses the nomenclature of Cotton.[7]

GROUP THEORY

The essential properties of a group are:

- The product of any two elements of a group is an element of the group. That is, if A and B are elements of a group, then AB is also an element of the group.
- One element of the group must commute with all others and leave them unchanged; that is, for every group there exists an element, E, such that for every element, A, of the group, $EA = A$.
- The associative law of multiplication; that is, $A(BC) = (AB)C$, holds.
- Every element must have a reciprocal, which is also an element of the group.

These properties are necessary and sufficient for a group to exist. For symmetry theory, as it applies to chemistry, the elements are symmetry operations, R_i. With this in mind, the essential parts of a chemical symmetry group are:

- The order, h, of a group, is the number of operations in the group.
- A pair of operations, A and B, are of the same class if there exists an operation X such that the relationship $B = X^{-1}AX$ holds.
- The order of a class, C, is the number of operations in the class.
- The number, n, of irreducible representations, Γ_j, of a group is equal to the number of classes.
- The degeneracy of irreducible representation Γ_j is l_j.
- The character of an operation, R_i, for irreducible representations, Γ_j, is χ_{ji}.

SYMMETRY OF UNIT CELLS

Symmetry operations on unit cells are, like those of a solid, the product of a point-group operation and a translation. Translations can be primitive, in which the system is translated through an integer number of unit cells, or nonprimitive, in which the translation is through a noninteger number of unit cells. Thus, the symmetry operation $\{C_6|0.5, 0\}$ involves rotation by 60° followed by translation through half a unit cell in the first translation direction. Any operation can be combined with a primitive translation to prevent an atom being moved out of the unit cell.

REPRESENTATIONS

In point-group theory, the symmetry-adapted representations, Γ_r, arising from various entities, such as atoms, atomic orbitals, or displacement vectors (for vibrational spectra), can be reduced to a set of irreducible representations. The number, m, of each type of irreducible representation present is given by:

$$m_i = \frac{1}{h}\sum_j^n C_j \chi_{ij} \chi_{rj} \qquad (1)$$

Depending on the types of entities involved, some or all of the irreducible representations may be generated. However, for the general point (i.e., a point that is not on any element of symmetry), every irreducible representation is generated when the associated symmetry adapted representation is reduced. In this case, all χ_{ji} are zero except for the identity, which is, in this case, equal to h, and eq. (1) collapses to a single quantity:

$$m_i = \frac{1}{h}\chi_{i1} \chi_{r1} = \frac{1}{h} l_i h = l_j \qquad (2)$$

That is, all irreducible representations can be generated by reducing the symmetry-adapted reducible representation of a random point. This fact is used as the basis for the generation of the characters of the irreducible representations.

The steps, then, in generating the character table are:

1. Generation of the operations of the symmetry group, followed by assignment of these operations to classes. This gives the order of the group.
2. Symmetry-adapted reducible representations are then produced, which can be reduced to an irreducible set. All the nondegenerate irreducible representations are then used, along with one member of each degenerate representation, in the construction of the character table.
3. The various characters are produced by operating on the representations with the operations of the group.

GENERATION OF CLASSES

For the topology under investigation, a general point in Cartesian space, X, is selected, in general, the point $(3, 5, 7)$ is convenient. Enough equivalent point are generated from this point to create the symmetry of the desired topology. There will be exactly h of these points. As an example, the topology, T, of the point group O_h can be generated by the permutations shown in eq. (3), in which P is the permutation operator.

$$T = P[\pm 3, \pm 5, \pm 7] \tag{3}$$

Before the procedure for identifying the operations of the system is started, some elements of symmetry in the topology are identified. These are needed for the construction of some operations. In the case of O_h, the essential elements of symmetry are a point, the origin $[(0, 0, 0)]$, three axes $[(0, 0, 1)$, $(1, 1, 0)$, and $(1, 1, 1)]$, and two planes of symmetry $[(x, 0, 0)$ and $(x, x, 0)]$.

Using the general starting point, X, the known operations of the group are performed. For a new group, the only operation initially known to exist is the identity, E, which leaves X unmoved. By inspection, a second operation is identified and used. This operation will move X to some other location. By repeated application of the operation, more general points are reached. New operations are readily identified as those operations that move X to a new point. If not all points are reached, which is likely, then another class of operation necessarily must exist. An operation that moves X to one of the remaining points is constructed and added to the set of classes. By repeated application of this operation, both with itself and with the operations already identified, more general points are reached. This process is repeated until all h operations and n classes are identified.

Either during the generation of operations or afterward, the operations can be assigned to classes. Because the only operations supplied to this procedure are representatives of the various classes, the assignment of operations to classes is most conveniently done when a new operation is generated.

The only step in this sequence that is not automatic is the generation of operations for new classes. However, by using the elements of symmetry, the symmetry operations can usually be easily identified.

GENERATION OF EIGENVECTORS

Eigenvectors are routinely generated in quantum-chemical calculations. These eigenvectors naturally transform as irreducible representations. For any given system, some or all of the irreducible representations may be present. However, to generate all the irreducible representations, it is not necessary to carry out a quantum-chemical calculation. In place of the secular determinant found in quantum-chemical calculations, any general secular determinant will suffice.

Construction of a general secular determinant is straightforward. For a given topology, a matrix of size h is constructed. Each off-diagonal element of the matrix represents the interaction of two general points in the topology, and the diagonal terms represent the interaction of a point with itself. The starting values for the interactions are quite unimportant, other than there should be no relationship between them. Because of this, it is convenient to set each element of the matrix to the value given by a random number generator:

$$H'_{\lambda\sigma} = \mathrm{RAN}(\lambda, \sigma) \tag{4}$$

This matrix is then symmetrized in two steps. First, the matrix is rendered symmetric:

$$\sum_{\lambda < \sigma} H'_{\lambda\sigma} = H'_{\sigma\lambda} \tag{5}$$

Then the matrix is subjected to the various operations of the group:

$$H = \frac{1}{h} \sum_i R_i H' \tag{6}$$

The result of this procedure is to generate a matrix, H, that has the same symmetry as that of the topology. Because the topology is that of a general point, diagonalization of the matrix yields a set of eigenvectors that spans all the irreducible representations of the associated group.

PROPERTIES OF EIGENVECTORS

The eigenvectors resulting from diagonalization of a symmetry-adapted matrix are symmetry adapted, which implies that they transform as the degenerate and nondegenerate irreducible representations of the group. Degenerate eigenvectors are characterized by the existence of two or more eigenvectors that have the same eigenvalue. In

symmetry theory, such sets of eigenvectors can be regarded as a single vector, in which the individual eigenvectors are merely components of the degenerate manifold. The symmetry properties of these vectors can be determined by evaluating the expectation values of the various operators:

$$\chi^{(ij)} = \langle \psi_i | R_j | \psi_i \rangle \tag{7}$$

Because the vectors are symmetry adapted, they transform as the irreducible representations; therefore, the expectation values generated by eq. (7) are the same as the characters of the various irreducible representations. For example, for degenerate vectors, the effect of the identity operation is to do nothing. Because the eigenvectors are normalized, the expectation value of the identity operation is 1.0 for each component, so the character of the identity operation is the same as the degeneracy of the irreducible representation.

After all the characters for all the vectors have been evaluated, the character table can be constructed. The totally symmetric representation, that is, the representation for which all the characters are 1, is identified, which is defined as the first irreducible representation. This is followed by the remaining nondegenerate representations. Care must be exercised when the degenerate representations are being constructed, because more than one vector will have the same symmetry. In fact, the number of vectors that have the same symmetry will be equal to the degeneracy. With this in mind, the remainder of the character table is constructed, typically in order of increasing degeneracy.

PROOF OF GROUPS

To prove that the structures generated by this procedure are indeed groups it is sufficient to show that they satisfy the conditions for a group, as given earlier. For cluster groups, all the operations can be represented by a 3×3 unitary transform combined with a nonprimitive translation. Using these structures, it is easy to show that the product, associative, and reciprocal relations exist for all operations. From this, it follows that the structures are indeed groups.

More interesting, however, are several of the properties of irreducible representations. Irreducible representations form an orthogonal set, as shown in eq. (8) and the sum of the squares of the degeneracies is h; that is:

$$\sum_R^h \chi_i(R)\chi_j(R) = \sum_A^n C_A \chi_i(A)\chi_j(A) = h\delta(i, j) \tag{8}$$

$$\sum l_i^2 = h \tag{9}$$

A consequence of the orthogonality of the representations is that the characters for the operations form an orthogonal set:

$$\sum_i^n \chi_i(R_A)\chi_i(R_B) = \frac{h}{\sqrt{C_A C_B}}\delta(A, B) \tag{10}$$

Application to Hexagonal Lattice

The application of the methodology just outlined can be illustrated using the two-dimensional graphite lattice. The space group of graphite is C_6/mmc; however, for the purposes of this discussion, only the two-dimensional hexagonal lattice structure will be used. This is easier to use than the full three-dimensional structure in illustrating the examples, and extension of the method of three dimensions is straightforward. In this system, the fundamental unit cell is C_2. Examples of cluster groups using both the fundamental unit cell and compound unit cells (i.e., finite objects in an infinite lattice) will now be presented.

GROUP OF TWO LATTICE POINTS

The fundamental unit cell in the two-dimensional hexagonal lattice is shown in Figure 1. This consists of two adjacent points, **A** and **B**, each of which is connected to two other points. The site symmetries at various points in the lattice are of interest. Two of the most important site symmetries are at the points themselves and at the center of the hexagon. For points **A** and **B**, the site symmetries are the same, C_{3v}. In the full three-dimensional lattice, the site symmetry would be D_{3h}, but because the third dimension is not being considered here, the symmetry decreases to C_{3v}, which reflects the fact that there is no symmetry attributed to the direction perpendicular to the lattice plane. Not all sites correspond to atom positions. Thus, the site of highest symmetry for example, is found at the center of each hexagon, where there are no atoms. This site has the point-group symmetry C_{6v}.

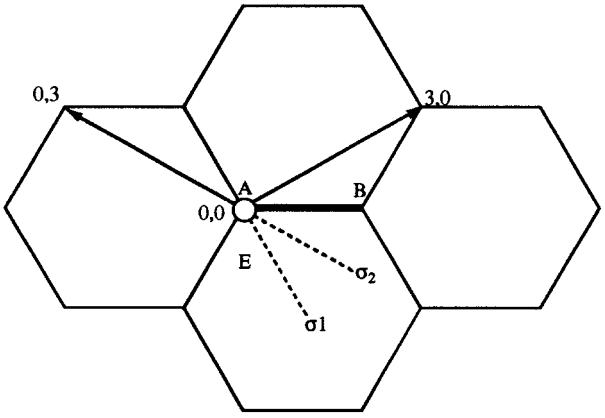

FIGURE 1. Symmetry elements used for line in hexagonal lattice.

The distinguishing feature of lattices is the presence of translational symmetry, the existence of which allows translational symmetry operations. In Figure 1 these are indicated by the two arrows.

To construct the symmetry group, the operations of the unit cell must first be identified. Although there is no theoretical requirement that all point-group operations must be performed at the same site, the use of a single site for these operations makes visualization of the operations considerably easier. For this system, the site selected is the location of point **A**. The effects of the various symmetry operators acting on a general point, also near to **A**, are shown in Figure 2. Three purely point-group operations, E, C_3, and σ_1, move the point to an equivalent point: the identity operation leaves the point unmoved; the C_3 operation rotates the point 120° in a counterclockwise direction; and the σ_1 operation reflects the general point through the symmetry plane σ_1 as shown in Figure 1. The remaining equivalent general points near to **A** can be reached by repeated application of these operations. To move the general point to the equivalent points around atom **B**, point group operations must be combined with nonprimitive translation operations. These operations move a point through a fraction of the unit cell dimensions. By defining the length of the unit cell as 3, the translation operations can conveniently be expressed as integers. Thus, point **A** can be translated to point **B** by translation through one third of a unit cell in the first direction, followed by translation through two thirds of a unit cell in the second direction. This places point **A** at point **B**, albeit in a different unit cell. The effect of the operation $\{E|1,2\}$, then, is to translate point **A** to point **B**. This is, however, not an allowed operation, because the effect of the same operation on point **B** would be to place it in the center of an adjacent hexagon. The operations that move a general point near **A** to an equivalent point near **B** are $\{C_2|1,2\}$, $\{C_6|1,2\}$, and $\{\sigma_2|1,2\}$. The remaining equivalent points can then be generated by repeated application of the already described operations.

For this system, there are 12 equivalent positions: 6 for each lattice point, and 6 classes of operation; thus, there are 6 irreducible representations. These are presented in the form of a character table in Table I. The order of the classes and the characters of the representations are identical to those of point-group C_{6v}. To emphasize the similarity, the names of the irreducible representations have been selected to be the same as those used in group C_{6v}.

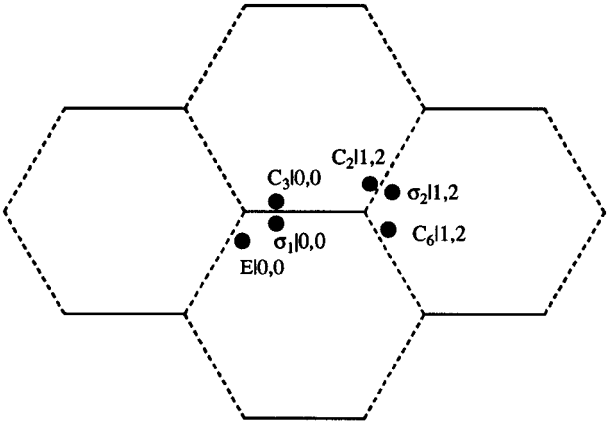

FIGURE 2. Symmetry operations for line.

TABLE I.
Symmetry Group for Two Adjacent Points in Hexagonal Lattice.

Order	1	2	3	1	2	3
Point	E	C_3	σ_1	C_2	C_6	σ_2
NPT	0, 0	0, 0	0, 0	1, 2	1, 2	1, 2
A_1	1	1	1	1	1	1
A_2	1	1	1	−1	−1	−1
B_1	1	1	−1	1	1	−1
B_2	1	1	−1	−1	−1	1
E_1	2	−1	0	2	−1	0
E_2	2	−1	0	−2	1	0

Point: point group operation; NPT: nonprimitive translation.

GROUP OF SIX LATTICE POINTS

The next system consists of a compound unit cell, constructed out of a cluster of six points forming a regular hexagon. This unit cell has high intrinsic symmetry, C_{6v}. For this unit cell, the center of the cluster is an obvious choice for the location of the symmetry site about which point-group operations are to be performed. Some of the elements of symmetry at this site are indicated in Figure 3. As a result of the existence of these elements, various symmetry operations also exist; representatives for each class are shown in Figure 4. Because all nonprimitive translation operations involve integer multiples of one third of the unit cell translation vector, the length of this vector is, for the sake of convenience, set to three.

Five of the symmetry operations, $\{E|0,0\}$, $\{C_2|0,0\}$, $\{C_3|0,0\}$, $\{\sigma_1|0,0\}$, and $\{\sigma_3|0,0\}$, do not involve nonprimitive translations. The effect of these operations is identical to the equivalent operations in point-group C_{6v}. One of these, $\{E|1,1\}$, involves only a nonprimitive translation. Finally, three operations, $\{C_6|1,1\}$, $\{C_3|1,1\}$, and $\{\sigma_2|1,1\}$, involve combinations of point-group operations and nonprimitive translations. Operation $\{C_6|1,1\}$, for example, can be regarded as operation $\{C_6|0,0\}$; that is, a counterclockwise rotation by 60° of the general point about the center of the hexagon, followed by the operation, $\{E|1,1\}$.

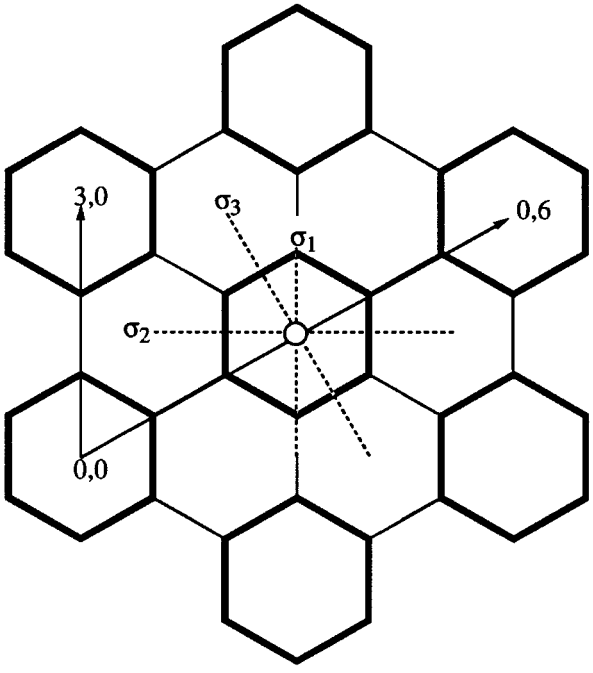

FIGURE 3. Symmetry elements used for hexagon in lattice.

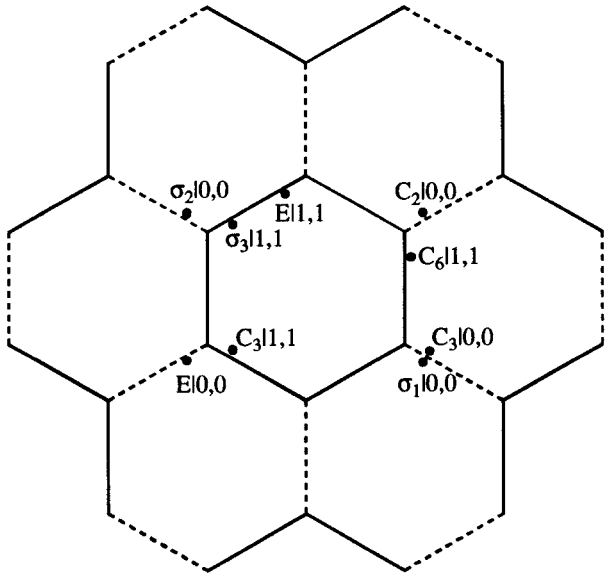

FIGURE 4. Symmetry operations of hexagon in lattice.

Each lattice point contributes 6 general points; therefore, there are 36 general points in all. All these points can be generated by the operations of the group, as a result the order of the group is 36. The group is shown in Table II.

This group is unlike any point group. Only the two simple point groups of the icosahedron, I and I_h, contain fourfold degenerate representations, and the current group is clearly different. Some exotic groups, such as the cubic double groups, also contain fourfold degeneracies, but, again, these are quite different from the current group. Therefore, the new group is different from all point-groups.

TABLE II.
Symmetry Group for a Hexagon in Hexagonal Lattice.

Order	1	2	9	3	6	3	2	4	6
Point	E	C_3	σ_1	C_2	C_6	σ_2	E	C_3	σ_3
NPT	0, 0	0, 0	0, 0	0, 0	1, 1	0, 0	1, 1	1, 1	1, 1
A_1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	−1	−1	−1	1	1	−1
B_1	1	1	−1	1	1	−1	1	1	−1
B_2	1	1	−1	−1	−1	1	1	1	1
E_1	2	−1	0	2	−1	0	2	−1	0
E_2	2	−1	0	−2	1	0	2	−1	0
E_3	2	2	0	0	0	2	−1	−1	−1
E_4	2	2	0	0	0	−2	−1	−1	1
G	4	−2	0	0	0	0	−2	1	0

The order of the group is finite, unlike the space groups, and is therefore different from the space groups.

In group theory, the order in which the classes of operation are presented is not important, although the identity operation universally comes before any other operation. Nor is the order of the irreducible representations important, although the totally symmetric representation is usually first. However, by suitably arranging the classes and representations, a subgroup can be constructed that has the same characters as that of the two points discussed earlier. That is, the group of the hexagon contains the group of the two points.

Because of the novelty of these new groups, there are no conventions for labeling the new irreducible representations. Nevertheless, because twofold degenerate representations are normally written as ''*E*,'' and fourfold as ''*G*,'' these symbols are used here.

GROUP OF 24 LATTICE POINTS

The next group is that of 24 points. This system can be represented as the highly symmetric cluster (Fig. 5A) or as the equivalent system (Fig. 5B). For convenience, the geometry in Figure 5B will be used. To generate all the operations for this cluster, six new classes of operation were needed. These, together with representative symmetry operations for the other classes, are shown in Figure 6. A direct consequence of the existence of these extra classes is that the associated group (Table III) contains six new representations: four threefold degenerate representations and one sixfold degenerate.

This system corresponds to one of the systems investigated by Hosoya et al., in which they reported the presence of sixfold degenerate levels. In π calculations, accidental degeneracies sometimes occur due to the use of only nearest-neighbor interactions. In this case, the presence of a sixfold degenerate level can be predicted from symmetry theory. By examining the effect of the various operations on the 24 points, the reducible representation can be constructed. Only three of these operations have nonzero characters, $\{E|0,0\}$, $\{\sigma_1|0,0\}$, and $\{C_3|0,0\}$; therefore, only these operations need be examined.

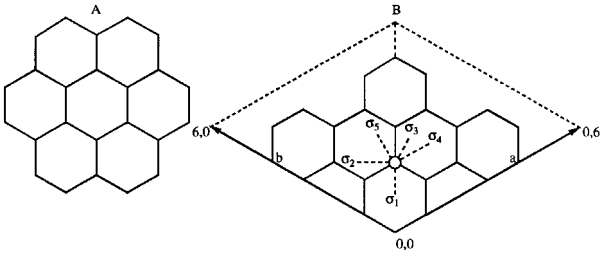

FIGURE 5. Symmetry operations of cluster of 24 points in hexagonal lattice.

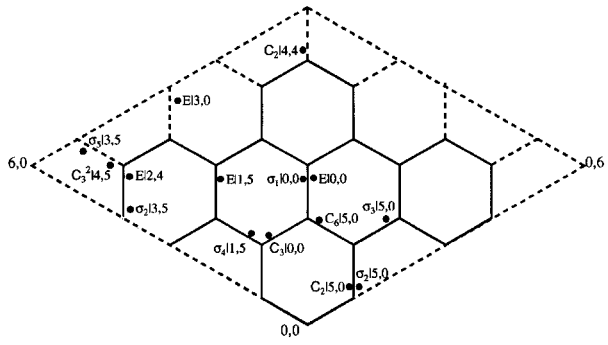

FIGURE 6. Symmetry operations of cluster of 24 points in lattice.

The effect of $\{E|0,0\}$ is to leave all points unmoved, so the character is 24. When the $\{\sigma_1|0,0\}$ operation is performed, four atoms are unmoved, and 20 atoms move, so the character for this operation is 4. The effect of the $\{C_3|0,0\}$ operation is not as obvious. One of the atoms is on the axis of rotation, and is, therefore, obviously unmoved. In point-group theory, all other atoms would be moved, and would as a result not contribute to the character. However, in the cluster group, two other atoms are unmoved. Consider atoms *a* and *b* in Figure 5B: Under the $\{C_3|0,0\}$ operation, these atoms would both move 120° counterclockwise, which would move them out of the unit cell. They could then be moved back into the unit cell by a primitive translation, which would place them in their original positions. Therefore, for the $\{C_3|0,0\}$ operation, the character is 3.

Given the reducible representation, the number of times the irreducible representation, χ_i, occurs can be calculated using eq. (1); for the totally symmetric representation:

$$m_1 = \frac{1}{144}(1 \times 1 \times 24 + 18 \times 1 \times 4 + 16 \times 1 \times 3) = 1 \quad (11)$$

When this operation is performed for all the irreducible representations, the set of 24 points can be shown to transform as $(A_1 + A_2 + G + T_2 + T_4 + \Gamma_{x1} + \Gamma_{x2})$, which is the precise set of degeneracies reported by Hosoya.

TABLE III.
Symmetry Group for 24 Points in Hexagonal Lattice.

Order	1	8	18	9	24	6	6	16	12	18	6	2	3	12	3
Point	E	C_3^2	σ_1	C_2	C_6	σ_2	E	C_3	σ_3	σ_4	σ_5	E	E	σ_3	C_2
NPT	0, 0	4, 5	0, 0	5, 0	5, 0	5, 0	1, 5	0, 0	3, 5	1, 5	3, 5	2, 4	3, 0	5, 0	4, 4
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	−1	−1	−1	1	1	−1	1	−1	1	1	−1	−1
B_1	1	1	−1	1	1	−1	1	1	−1	−1	−1	1	1	−1	1
B_2	1	1	−1	−1	−1	1	1	1	1	−1	1	1	1	1	−1
E_1	2	−1	0	2	−1	0	2	−1	0	0	0	2	2	0	2
E_2	2	−1	0	−2	1	0	2	−1	0	0	0	2	2	0	−2
E_3	2	2	0	0	0	2	−1	−1	−1	0	2	−1	2	−1	0
E_4	2	2	0	0	0	−2	−1	−1	1	0	−2	−1	2	1	0
G	4	−2	0	0	0	0	−2	1	0	0	0	−2	4	0	0
T_1	3	0	−1	−1	0	1	−1	0	−1	1	−1	3	−1	1	3
T_2	3	0	1	−1	0	−1	−1	0	1	−1	1	3	−1	−1	3
T_3	3	0	−1	1	0	−1	−1	0	1	1	1	3	−1	−1	−3
T_4	3	0	1	1	0	1	−1	0	−1	−1	−1	3	−1	1	−3
Γ_{X1}	6	0	0	0	0	−2	1	0	−1	0	2	−3	−2	1	0
Γ_{X2}	6	0	0	0	0	2	1	0	1	0	−2	−3	−2	−1	0

In the cluster of 24 points, the π-orbitals are totally symmetric; therefore, the above analysis can be performed by regarding each point as consisting of a single, symmetric, orbital. When a semiempirical cluster calculation on two-dimensional graphite is carried out, each point represents all orbitals on a carbon atom: that is, a basis set consisting of $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. Two of the atomic orbitals, the s and $p\pi$, transform as the simple points just described. The other two, the in-plane p orbitals, transform together.

The characters of the reducible representation for these two orbitals can be obtained as the product of the characters for the point-group and cluster-group operations. The characters for the point-group operations for the in-plane p orbitals are $\{E|0,0\}$: 2, $\{\sigma_1|0,0\}$: 0, and $\{C_3|0,0\}$: -1; therefore, the reducible representation is $\{E|0,0\}$: 48 and $\{C_3|0,0\}$: -3. From this it follows that, for the full basis set, the reducible representation is $\{E|0,0\}$: 96, $\{\sigma_1|0,0\}$: 144, and $\{C_3|0,0\}$: 48. When this is reduced, the set of irreducible representations for a cluster of 24 carbon atoms forming a unit cell having a coronene structure is seen to be $(2A_1 + 2A_2 + E_1 + E_2 + E_3 + E_4 + 3G + T_1 + 3T_2 + T_3 + 3T_4 + 4\Gamma_{x1} + 4\Gamma_{x2})$. Evidence that this set of representations is valid was provided by a single SCF calculation on a cluster of 24 carbon atoms. Examination of the eigenvalues revealed the following expected degeneracies: nondegenerate, 4; twofold, 4; threefold, 8; fourfold, 3; and sixfold, 8.

GROUP OF 72 LATTICE POINTS

The last group examined was the group of 72 points, forming a hexagonal unit cell, as shown in Figure 7A. Again, for computational convenience, the actual unit cell used was a symmetric parallelogram, Figure 7B. This cluster was chosen for study because of the postulated presence of a 12-fold degenerate level. When the cluster group was constructed (Table IV), this highly degenerate representation was indeed found.

Larger groups are predicted to contain more representations, but all additional representations would be related to the representations already identified. This situation is analogous to that found in the C_{nv} groups, in which the number of representations increases without limit as n increases; however, after the first few groups, the relationship of the new representations of those of lower groups is quite obvious. Likewise, in going to larger and larger clusters that have hexagonal symmetry, the number of 6- and 12-fold degenerate representations would steadily increase. For other clusters in the hexagonal lattice, more fourfold degenerate representations would be found.

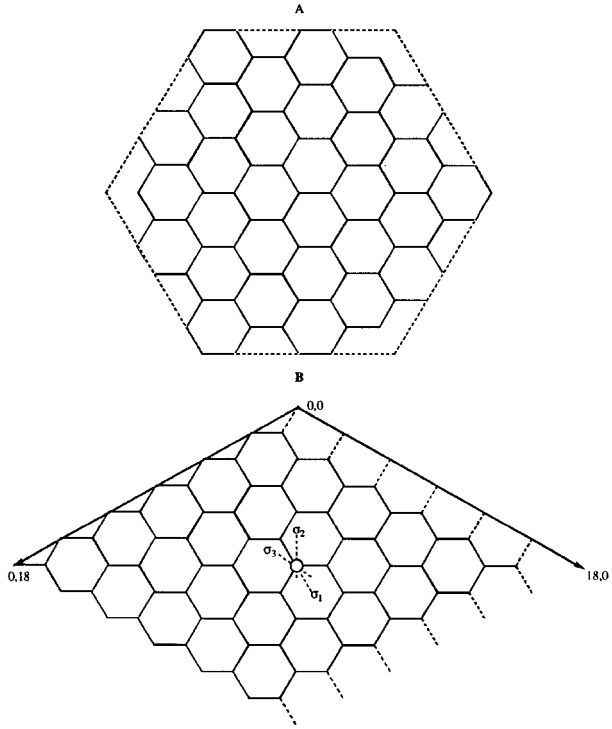

FIGURE 7. cluster of 72 points in hexagonal lattice.

Discussion

RELATIONSHIP BETWEEN NEW GROUPS AND POINT GROUPS AND BRILLOUIN ZONES

As has been shown, the cluster groups are not simply related to either point groups or to space groups. However, by examination of the irreducible representations, various relationships between the cluster groups and the other two types can be identified. As has been noted earlier, the irreducible representations for the cluster group for two points are similar to those in point group C_{6v}. With minor changes, these representations also appear in the other, larger cluster groups. When the nonprimitive translations are ignored, these other groups can be regarded as simply multiples of the cluster group of two points. Thus, the group of 72 points contains 36 operations of type E, 72 of type C_3, etc., that is, the six representations of the cluster group of two points have the same characters for the same operations regardless of the translational operations (Fig. 8). Only one

TABLE IV.
Symmetry Group for 72 points in the Hexagonal Lattice.

Order	1	24	18	27	72	18	6	48	36	36	18	6	3	36	9	6	12	2	36	18
Point	E	C_3	σ_1	C_2	C_6^5	σ_2	E	C_3	σ_2	σ_1	σ_3	E	E	σ_2	C_2	E	E	E	σ_1	σ_1
NPT	0, 0	3, 0	0, 0	1, 17	1, 2	7, 2	3, 0	0, 0	4, 2	3, 0	1, 2	6, 0	9, 0	1, 2	4, 14	6, 3	9, 3	12, 6	6, 0	9, 0
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_2	1	1	1	−1	−1	−1	1	1	−1	1	−1	1	1	−1	−1	1	1	1	1	1
B_1	1	1	−1	1	1	−1	1	1	−1	−1	−1	1	1	−1	1	1	1	1	−1	−1
B_2	1	1	−1	−1	−1	1	1	1	1	−1	1	1	1	1	−1	1	1	1	−1	−1
E_1	2	−1	0	2	−1	0	2	−1	0	0	0	2	2	0	2	2	2	2	0	0
E_2	2	−1	0	−2	1	0	2	−1	0	0	0	2	2	0	−2	2	2	2	0	0
E_3	2	2	0	0	0	2	−1	−1	−1	0	2	−1	2	−1	0	2	−1	2	0	0
E_4	2	2	0	0	0	−2	−1	−1	1	0	−2	−1	2	1	0	2	−1	2	0	0
G	4	−2	0	0	0	0	−2	1	0	0	0	−2	4	0	0	4	−2	4	0	0
T_1	3	0	−1	−1	0	1	−1	0	−1	1	−1	3	−1	1	3	−1	−1	3	−1	1
T_2	3	0	1	−1	0	−1	−1	0	1	−1	1	3	−1	−1	3	−1	−1	3	1	−1
T_3	3	0	−1	1	0	−1	−1	0	1	1	1	3	−1	−1	−3	−1	−1	3	−1	1
T_4	3	0	1	1	0	1	−1	0	−1	−1	−1	3	−1	1	−3	−1	−1	3	1	−1
Γ_{X1}	6	0	0	0	0	−2	1	0	−1	0	2	−3	−2	1	0	−2	1	6	0	0
Γ_{X2}	6	0	0	0	0	2	1	0	1	0	−2	−3	−2	−1	0	−2	1	6	0	0
Γ_{11}	6	0	2	0	0	0	4	0	0	1	0	0	−2	0	0	1	−2	−3	−1	−2
Γ_{12}	6	0	−2	0	0	0	4	0	0	−1	0	0	−2	0	0	1	−2	−3	1	2
Γ_{21}	6	0	2	0	0	0	0	0	0	−1	0	0	6	0	0	−3	0	−3	−1	2
Γ_{22}	6	0	−2	0	0	0	0	0	0	1	0	0	6	0	0	−3	0	−3	1	−2
Q	12	0	0	0	0	0	−4	0	0	0	0	0	−4	0	0	2	2	−6	0	0

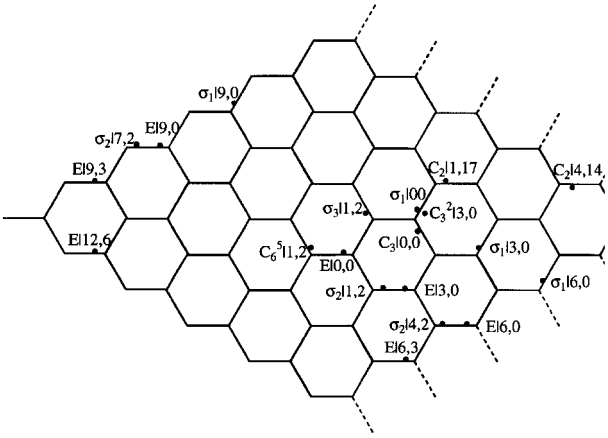

FIGURE 8. Symmetry operations of cluster of 72 points in hexagonal lattice.

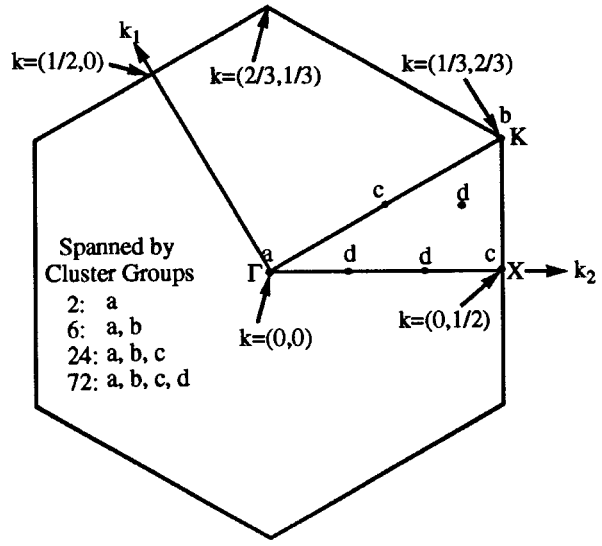

FIGURE 9. Representative points in Brillouin zone generated by cluster group of 72 points.

point in the Brillouin zone has this property, the Γ point; therefore, all the irreducible representations for the cluster of two points correspond to the Γ point in the hexagonal Brillouin zone.

The cluster group for the hexagon contains three additional representatives, E_3, E_4, and G. Assuming that these correspond to a different point in the Brillouin zone, the location of that point can be inferred from the characters of these representations under the operation $\{C_3|1,1\}$. For all three representations, the character is nonzero; therefore, these points must be located at a point in the Brillouin zone which has threefold symmetry. The only such point is at the vertex of the zone, so these three irreducible representations are located at point K in the hexagonal Brillouin zone (Fig. 9). Each Brillouin zone has six K points. However, each such point is shared by three Brillouin zones, so each Brillouin zone contains precisely two complete K points. Because of this, the irreducible representations at K have automatic twofold degeneracy. The small cogroup at K has C_{3v} symmetry, and this is reflected in the characters of the representations, as shown in Table V.

In going to the group of 24 points, six new representations are encountered. These correspond to the points X and the point midway between Γ and K. The small cogroup at X has C_{2v} symmetry, which is reflected in the characters for that point. Because each Brillouin zone contains three X points, the new irreducible representations all have intrinsic threefold degeneracy. The only element of symmetry available for the sixfold degenerate level is the mirror plane; therefore, the small cogroup for the sixfold degenerate level is C_s.

The results reported by Hosoya et al. can now be interpreted within the context of cluster groups. Their ''coronene torrus'' system corresponds to the cluster of 24 points used here. However, their ''points'' are somewhat simpler, corresponding to a symmetric orbital located on a lattice site rather than the aforementioned general points. Therefore, their secular determinant was of size 24. The locations in the Brillouin zone are independent of the complexity of the fundamental unit cell, so each location in the zone corresponds to precisely two points. This is, in fact, what was reported: the eigenvalues at ± 3 correspond to the irreducible representations at the Γ point, those at $K(0)$ were fourfold degenerate, those at $X(\pm 1)$ were threefold degenerate, and those halfway between Γ and $K(2)$ were sixfold degenerate.

Using Hückel theory, the eigenvalue spectrum of the graphite lattice has been expressed analyti-

TABLE V.
Comparison of C_{3v} Point-Group and Small Cogroup at K.

Point group C_{3v}				Small cogroup at K			
Class	1	2	3	Class	1	2	3
Point	E	C_3	σ_v	Point	E	C_3	σ_3
				NPT	0, 0	0, 0	0, 0
A_1	1	1	1	E_3	2	2	2
A_2	1	1	−1	E_4	2	2	−2
E	2	−1	0	G	4	−2	0

cally.[8] For the coronene structure, the associated multilayered cyclic fence graph is identified by the symbol $F_{2,6}$, and the eigenvalue spectrum is given very concisely by:

$$P_{F_{m,n}}(x) = \prod_{k=1}^{m}\prod_{j=1}^{n}\left\{x^2 - \left[3 + 2\cos\frac{2\pi j}{n} + 2\cos\left(\frac{2\pi j}{n} + \frac{2\pi k}{m}\right) + 2\cos\left(\frac{2\pi 2j}{n} + \frac{2\pi k}{m}\right)\right]\right\} = 0 \quad (12)$$

In this expression, the axis associated with j corresponds to a line in the Brillouin zone from Γ to K, and the axis associated with k makes an angle of 150° with j; that is, the coordinate (j, k) of K is $(2, 0)$, and X is $(0, 1)$. The points in the Brillouin zone for the $F_{2,6}$ fence graph generated by eq. (12) are shown in Figure 10. Inspection of these points and those in Figure 9 show that, although they were generated by very different methods, graph theory and symmetry theory, they are nonetheless completely equivalent. Using eq. (12), the Hückel eigenvalues for any cluster can be evaluated. The symmetry of the associated eigenvectors can then be determined by using the cluster group theory outlined here.

Six more irreducible representations are found in the cluster group for 72 points. These correspond to two sets of representations on the line Γ to X, and a 12-fold degenerate point that is not on any element of symmetry. The point-group symmetry on the line is C_s; therefore, the representations for the points on the line are either symmetric to the plane of symmetry, Γ_{11} and Γ_{21}, or are unsymmetric, Γ_{12} and Γ_{22}. The general point has

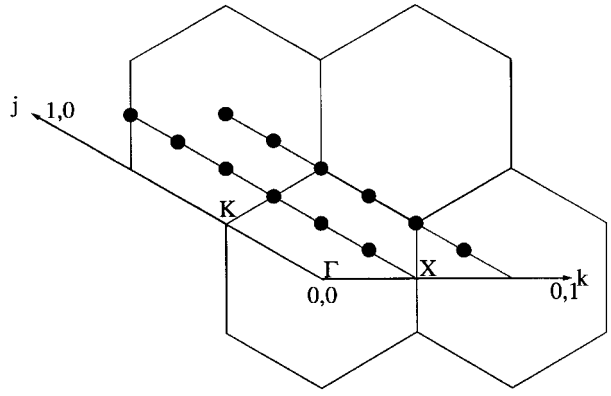

FIGURE 10. Points in Brillouin zone generated by eq. (12) for graph $F_{2,6}$.

no point group symmetry; therefore, the small group is simply C_1, which is reflected in the characters of the representation: the only operations for which the characters are nonzero are those that involve nonprimitive translations only. However, the general point has 12 equivalent positions, so the degeneracy due to translational symmetry is 12.

The locations in the Brillouin zone of all the irreducible representations of the group of 72 points are also shown in Figure 9. As has been shown earlier, the characters of the small cogroups can be related to those of the point groups. What is not so obvious is that the characters of those operations that involve nonprimitive translations can also be derived from the properties of the Brillouin zone. Consider the simple nonprimitive translations—that is, the operations $\{E|n, m\}$. The effect of these operations on the components, Ψ^a, of the representations can be calculated as:

$$\chi^a = \langle \Psi^a | \{E|n, m\} | \Psi^{a^*} \rangle \quad (13)$$

For a specific representation at the point (j, l) in the Brillouin zone, eq. (13) can be resolved to give:

$$\chi^a = e^{i2\pi jn}\, e^{i2\pi lm^*} \quad (14)$$

This quantity is, in general, complex. However, with the exception of the Γ point, for which the characters of the representations are real, all points in the zone have an equivalent point having coordinates that are negative values of those of the point. As a result, the character of any point, plus those of the equivalent point obtained by inversion through the center of the zone, are necessarily real. Because the real components are the same, only the real components of the unique equivalent points need be evaluated.

This can be demonstrated using the representations at K. From Figure 9, the coordinates of K are $(\frac{1}{3}, \frac{2}{3})$ and $(\frac{2}{3}, \frac{1}{3})$. Consider now the operation $\{E|6, 2\}$ (Fig. 8). This moves each lattice point two units of the fundamental unit cell in the first translation direction followed by one unit in the second direction. For this operation, the characters of the two points are:

$$\chi^1 = e^{i2\pi\frac{1}{3}2}\, e^{i2\pi\frac{2}{3}1^*} = e^{i\pi\frac{4}{3}}\, e^{i\pi\frac{4}{3}^*} = 1$$
$$\chi^2 = e^{i2\pi\frac{2}{3}2}\, e^{i2\pi\frac{1}{3}1^*} = e^{i\pi\frac{8}{3}}\, e^{i\pi\frac{2}{3}^*} = 1 \quad (15)$$

In a similar manner, all characters for the $\{E|n, m\}$ operations for all representations in Table IV can be generated. For the remaining characters values can be calculated by combining the effect

of point-group operations and nonprimitive translation.

As has been shown, the degeneracy of a representation increases as the site symmetry in the Brillouin zone decreases, until, at the general point, the degeneracy of the representation equals the order of the point group to which the Brillouin zone belongs. In the case of the hexagonal two-dimensional Brillouin zone, this is 12. The highest point group symmetry for any Brillouin zone occurs in the cubic space groups. For such zones, the degeneracy of the general point equals that of the order of the group O_h; that is, 48. If the procedure outlined here were applied to a general point in a cubic lattice, using a cubic unit cell composed of 343 fundamental unit cells, then the associated cluster group would contain one 48-fold degenerate irreducible representation. Of all the finite symmetry groups used in chemistry, this is likely to be the group with the highest degeneracy.

Only a few groups have been reported in the present study. The total number of cluster groups possible is obviously infinite. Clearly, a new group can be constructed for every new unit cell. However, as mentioned earlier, beyond a certain point the amount of new information provided by a cluster group drops sharply. The point at which this occurs can be identified as follows: With an increasing size of unit cell, the potential number of small cogroups of the associated space group increases. The largest cluster group could then be defined as the group corresponding to the smallest unit cell that includes all small cogroups, including the general point, in the Brillouin zone. The total number of such cluster groups is likely to be quite large, probably in the low thousands.

As a consequence of their close relationship to both point groups and space groups, the cluster groups should be regarded as a third kind of group that is intermediate between point and space groups.

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